

RESEARCH ARTICLE

Unlocking Inert Material to Durable Cathode for Magnesium Storage Inspired via Synergistic Spin-Orbital Reconfiguration and Adaptive Crystal Transformation

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ABSTRACT

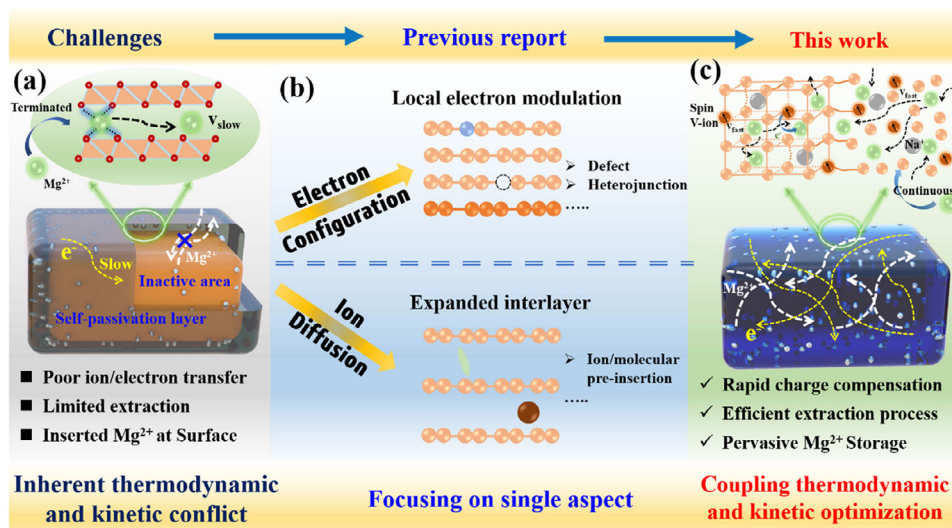
High polarity of Mg²⁺ results in unsatisfied interactions with the cathode host lattice, giving rise to sluggish Mg²⁺ diffusion and thus surface “self-passivation” caused by irreversible insertion/extraction of Mg²⁺, impeding development of magnesium metal batteries (MMBs). Herein, we pioneer a Defect Chemistry-Inspired synergistic strategy of synchronously Spin-State Modulation and Adaptive Microstructural Reformation, thereby resolving the inherent thermodynamic–kinetic conflict to improve Mg²⁺ storage. Combining first-principles calculations with advanced characterization, the intrinsic inertness of the V-3d⁰ orbital in Cu₃VS₄ was activated by filling electrons to induce a spin state change after introducing Na⁺, which enhanced the electron hopping process for rapid charge compensation to unlock Mg²⁺ storage ability. Furthermore, the cathode undergoes a self-driven structural evolution into a microcrystalline/amorphous hybrid, improved the cathode-electrolyte interface and Internal reaction site to balance subsequent Mg²⁺ adsorption and mobility. The optimized material, C@A-N-0.5, delivers a high specific capacity of 140 mAh g^{−1} at 40 mA g^{−1} (92% of capacity over rarely reported 300 cycles), and it had over 100 mAh g^{−1} at 200 mA g^{−1} for 1000 cycles, far outperforming the unmodified Cu₃VS₄ with negligible Mg²⁺ storage. This work provides mechanistic insights and materials design pathways for high-performance MMBs cathodes based on transition metal sulfides.

1 | Introduction

Beyond the state-of-the-art lithium-ion battery technology, rechargeable Magnesium Metal Batteries (MMBs) have garnered significant interest due to the high theoretical capacity from the two electrons transfers of Mg²⁺/Mg⁰ and the abundance of

magnesium, etc [1–6]. Even so, advancing cathode materials that facilitate fast and reversible Mg²⁺ insertion/extraction remains a major scientific challenge. An unsuitable electronic structure can trigger unfavorable Mg²⁺ insertion and subsequent diffusion behavior, resulting in an inherent mismatch between the thermodynamic stability and kinetic mobility of the intercalation

Wenwei Zhang and Zenan Xu contributed equally to this work.



SCHEME 1 | (a) Challenges faced by magnesium storage cathode materials. (b) Existing modification strategies for improving Mg^{2+} storage ability [10–20]. (c) Schematic diagram of the Mg^{2+} storage process after synergistic ion/electron regulation.

process [7–9]. As shown in Scheme 1a, the unsatisfied electrostatic interaction and slow charge compensation hinder further diffusion into the bulk or extraction during dis./charging process, leading to the formation of a passivation layer on the surface after Mg^{2+} inserts into the near-surface region during initial cycles, reduced utilization of active material, and capacity fade.

From the electronic structure perspective, the Mg^{2+} insertion energy and migration behavior are essentially related to the electronic states near the Fermi level of the host and electron density distribution of the bulk lattice tunnel [16, 21]. An ideal cathode material should possess suitable unoccupied electronic states to effectively accept electrons upon Mg^{2+} insertion, enabling smooth charge compensation and resulting in thermodynamically moderate adsorption strength. Common strategies for electronic structure modulation include constructing heterojunctions and defect engineering, etc [22–27]. For instance, studies have shown that single-atom Cu doping in MoS_2 can enhance electron transport and strengthen Mg^{2+} adsorption, achieving high reversible capacity [13]. This was also reported to introduce Se into $Cu_{1.8}S_{1-x}Se_x$ can modulate the chemical environment of Cu, thereby improving reaction kinetics [15]. Nevertheless, while these strategies primarily optimize adsorption behavior, the effect on modulating Mg^{2+} diffusion pathways remains limited (Scheme 1b).

Additionally, regarding the ion transport mechanism, an ideal Mg^{2+} storage structure should support efficient ion migration and mitigate stress induced by insertion/extraction. Diffusion kinetics depend sensitively on the local electronic environment at the migration transition state. Mg^{2+} migration faces a high electrostatic barrier when the material is insulating or has highly localized electronic states. Furthermore, in crystalline materials, ions typically diffuse along limited and directional channels, where channel blockage or structural deformation can severely hinder ion transport. The current primary approach is to enlarge the interlayer spacing to increase the distance between Mg^{2+} ions and anions, thereby decreasing the Coulombic interactions

with the aim of promoting rapid Mg^{2+} diffusion (Scheme 1b) [14, 18, 20, 28]. However, current research often focuses on a single aspect, and systematic studies aimed at synchronously optimizing ion/electron transport channels and elucidating the underlying mechanisms remain scarce.

Therefore, one of the pivotal challenges in achieving high-performance MMBs lies in designing cathode materials with synergistic ion/electron transport capabilities. The key is to synchronously achieve moderate adsorption energy and low diffusion energy barriers, thereby balancing thermodynamic advantages and kinetic efficiency. Typically, d^0 transition metal compounds (including empty d orbital, like Cu_3VS_4 , WO_3 , MoO_3 , and V_2O_5 , etc.) exhibit stable crystal structures and principal long cycle life, as their empty d-orbitals inhibit Jahn-Teller distortion and facilitate strong anion bonding. However, this electronic structure precludes d–d electron transition pathways, leading to low intrinsic conductivity and poor rate performance [29]. Additionally, the rigid framework experiences significant stress upon the insertion of the highly polarizing Mg^{2+} , limiting its practical application. Therefore, a fundamental understanding and precise control of the Mg^{2+} storage properties in these materials are crucial.

Based on the above discussion, as shown in Scheme 1c with a focus on Cu_3VS_4 as a representative material, this research proposes Na^+ pre-intercalation into Cu_3VS_4 to modulate its electronic structure, combined with first-principles calculations to deeply investigate the mechanism of how electronic restructuring affects magnesium storage behavior. Furthermore, an adaptive electrochemical reconstruction strategy is employed to construct a microcrystalline/amorphous cathode material, and its structure and micro-crystallization evolution are systematically analyzed using advanced characterization techniques. Finally, the effectiveness of the proposed synergistic electronic/ionic modulation strategy is validated based on theoretical calculations and electrochemical performance tests. This study provides new ideas and experimental evidence for achieving efficient Mg^{2+} storage.

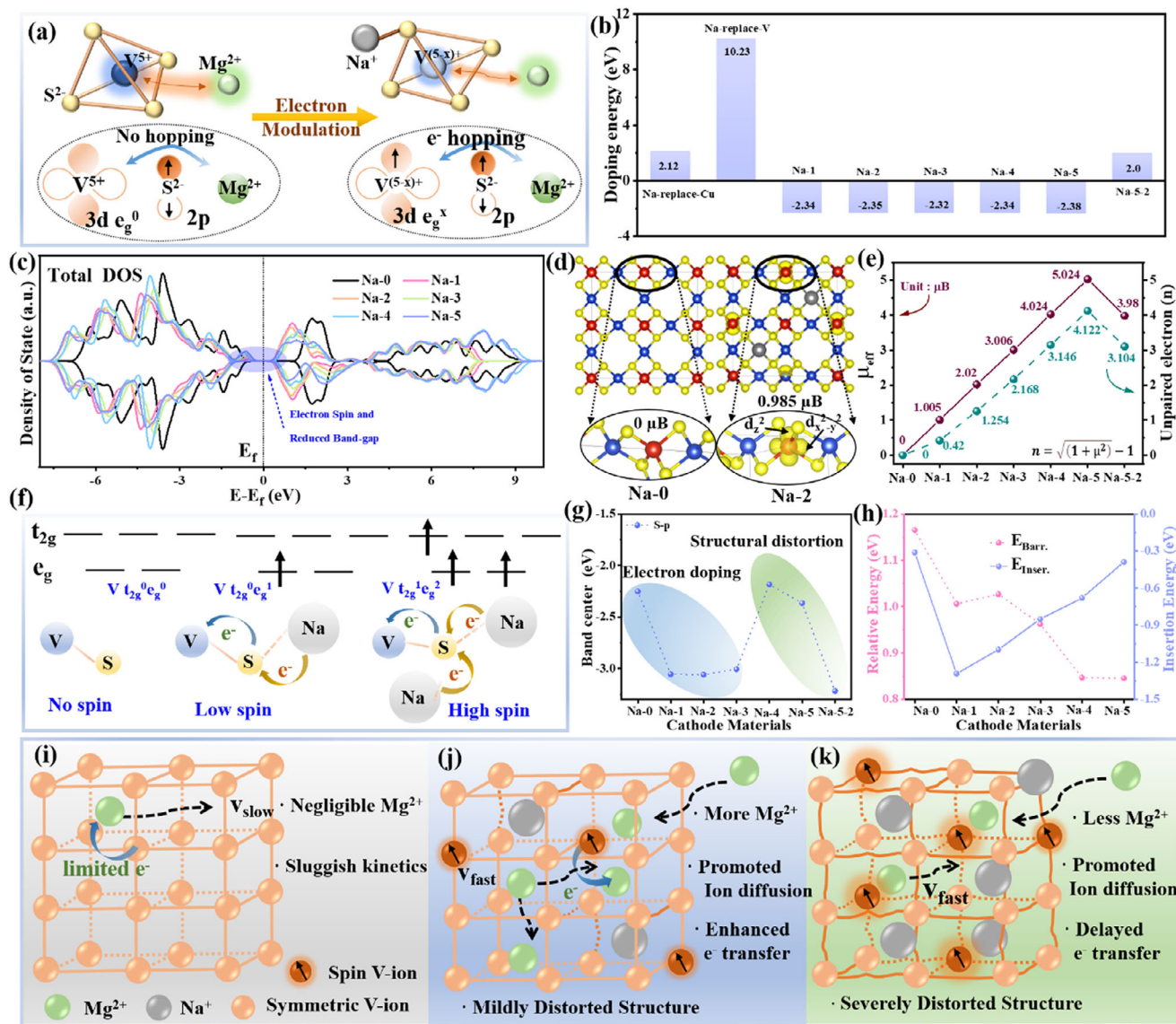


FIGURE 1 | (a) Schematic diagram of electron exchange in the Mg^{2+} environment with different valence states of V. (b) Doping energy at different Na^+ ion doping sites. (c) Total density of states under different concentrations of Na^+ doping. (d) Electron spin density diagrams for the Na-0 and Na-2 models. (e) Magnetic moment values of V and the number of lone electrons at different concentrations of Na^+ doping. (f) Schematic diagram of the spin configuration. (g) p-band center of S at different concentrations of Na^+ ion doping. (h) Variation of doping energy and diffusion barrier of Mg^{2+} ions at different concentrations of Na^+ doping. (i–k) Schematic illustration of the structural evolution and the corresponding impact on the Mg storage process in pure, low-concentration, and high-concentration Na^+ -doped Cu_3VS_4 , respectively.

2 | Result and Discussion

2.1 | Reaction Mechanism Design

As depicted in Figure 1a, in pristine Cu_3VS_4 , each vanadium ion is coordinated by four sulfur ions, forming isolated $[\text{VS}_4]$ units with a tetrahedral geometry. The higher electronegativity of sulfur relative to vanadium drives electron transfer from V to S, resulting in empty V-d orbitals and a formal oxidation state of V^{5+} . This high oxidation state of V^{5+} induces strong Coulombic repulsion against Mg^{2+} ions within the framework, impeding their insertion into the host structure. Moreover, there is a high-energy level of t_{2g} and a low-energy level of e_g in $[\text{VS}_4]$ units according to the Crystal Field Theory, the empty-orbital of V^{5+} (d^0 configuration) renders

the electron hopping process, further hindering efficient charge transfer during cycling and leading to sluggish ion diffusion and slow overall reaction kinetics [30, 31]. In principle, the pre-inserted Na^+ is expected to alter the electron configurations of S^{2-} and V^{5+} . This process fills electrons into the V-3d orbitals for electric neutrality, thus enabling a charge exchange process with V-ions upon Mg^{2+} intercalation and releasing the Coulombic repulsion. Additionally, the large ionic radius of Na^+ (0.102 nm) can enlarge the lattice and facilitate the Mg^{2+} diffusion process.

Based on this analysis, comprehensive density functional theory (DFT) calculations were carried out to predict the potential structure and effect of Na^+ doping on the electronic structure reconfiguration of Cu_3VS_4 . Several models of Na^+ -doped Cu_3VS_4

were constructed, and the corresponding Na⁺ doping formation energies were calculated. As shown in Figure 1b and Figures S1 and S2, the doping energies for Na⁺ substituting Cu and V lattice sites are 2.12 and 10.23 eV, respectively, indicating that both substitution processes are energetically unfavorable, especially at the V site. In contrast, interstitial incorporation of Na⁺ is relatively more feasible, as represented by several optimized configurations (labeled as Na-0, Na-1, Na-2, Na-3, Na-4, and Na-5). Given that both Na⁺ and Cu⁺ possess a +1 valence state, we also examined the possibility of Na⁺ replacing Cu⁺ at interstitial sites under varying doping concentrations (Figure S3). After structural optimization, it was observed that in all configurations except one structure, where the Cu⁺ at site 2 in Na-4 is replaced by Na⁺ (denoted as Na-5-2), the introduced Na⁺ migrated from lattice sites to interstitial positions. Moreover, in the Na-5-2 configuration, the doping energy for Na⁺ substituting Cu⁺ is 2.0 eV, which is lower than that of the interstitial doping case (Na⁺ replaces Cu⁺ in Cu₃VS₄, 2.12 eV in Figure 1b). These results suggest that Na⁺ tends to occupy interstitial sites preferentially, but can also potentially replace Cu⁺ under specific conditions.

Subsequently, the electron localization function (ELF) is used to evaluate the electron distribution around individual atoms (Figures S4 and S5). After introducing Na⁺ into Cu₃VS₄, the symmetric charge distribution around S and V is disrupted and accompanying with the increased charge density, which indicates that the doped Na⁺ leads to the excess electron around the V-3d and S-2p orbitals. However, compared to Na-5, the charge distribution in Na-5-2 exhibits an opposite trend, possibly due to a saturation effect of Na⁺ incorporation or a different local coordination environment, which will be further discussed in a subsequent section.

Furthermore, Bader charge analysis (Figure S6) reveals that as the Na⁺ concentration increases, the S-ions gain more electrons, while the V ions lose progressively fewer electrons. In contrast, the Cu-ions show less change due to their fully occupied d-orbitals. These observations reflect a general decrease in the valence states of the host ions upon Na⁺ incorporation. However, in comparison with Na-5, the Bader charges of Na-5-2 indicate that the S-ions gain fewer electrons, whereas the V and Cu-ions lose more electrons, suggesting an increase in the valence of these metal elements. This trend is attributed to severe structural distortion resulting from the large difference in ionic radii between Na⁺ and Cu⁺ after Na⁺ substitution. And the difference in electronegativity between Na and Cu (0.93 vs. 1.90) could induce the reshuffling of electron density.

A more detailed examination of the density of states (DOS) reveals that, compared to Na-0, the Na-x configurations exhibit significantly reduced band gaps and the emergence of spin-polarized states at the valence band maximum, which may predict varied electron transfer processes for differentiating Mg²⁺ storage ability (Figure 1c) [32–34]. Projected density of states (PDOS) analysis (Figures S7–S9) indicates that this is primarily due to the filling of unpaired electrons into the V-3d e_g orbitals, particularly the d_{z²} orbital, which leads to spin polarization after Na⁺ doping. In Na-5, however, excessive Na⁺ introduction causes additional electron occupation in the higher-energy d_{xy} orbital. Consistent with the charge analysis above, Na-5-2 again shows a distinct electronic structure (Figure S10), where electron occupation is exclusively

observed in the d_{z²} orbital. Furthermore, the electron spin density results confirm that Na⁺ doping introduces electron filling on the V-ions and the single-electron occupancy mainly in d_{z²} and then d_{xy} orbitals, which is usually accompanied by corresponding changes in magnetic moment (Figure 1d; Figure S11) [35]. As shown in Figure 1e, the number of unpaired electrons, derived from the total magnetic moment of V, shows a trend consistent with the above results. Based on these findings, the typical corresponding electron spin configurations were proposed for different contents of Na⁺ ions (Figure 1f). Specifically, the d orbitals of V contain no electrons in Na-0, electrons preferentially occupy the lower-energy e_g orbitals at low Na⁺ doping concentrations, and unpaired electrons also appear in the higher-energy t_{2g} orbitals at higher concentrations.

Accordingly, the calculated S-p-band center shows a distinct evolution with Na⁺ doping, and it downshifts in Na-1, Na-2, and Na-3 compared to pristine Na-0, but upshifts abruptly in Na-4, Na-5, and Na-5-2 (Figure 1g). This non-monotonic trend is attributed to the competition between the electron-doping effect at low concentrations and the structural distortion effect at high concentrations. Since the S-p-band center is a key descriptor of the host-guest interaction, this variation is expected to significantly influence the subsequent Mg²⁺ storage properties. To verify this, the Mg²⁺ insertion energy and diffusion barrier were calculated for these potential models (Figure 1h; Figures S12–S16). The results show that the diffusion barrier gradually decreases from 1.17 eV in Na-0 to 0.85 eV in the Na-5 series. Concurrently, the insertion energy increases (becomes less negative) from −1.29 eV in Na-1 back to −0.39 eV (equivalent to the value of −0.31 eV for Na-0). According to the further PDOS analysis in Figure S17, compared to the Mg-s to S-p orbital in Na-0, there is more orbital overlap in Na-2, which was mainly contributed by the introduction of Na⁺ for altering the electron structure [36]. Thus, the latter had more negative insertion energy than that of the former, and this result indicates that an optimal Mg²⁺ insertion energy is achieved only with a moderate level of Na⁺ doping. Notably and differently, while Na-5-2 exhibits a more negative Mg²⁺ insertion energy (−0.56 eV) than Na-5 (−0.39 eV) due to the electron reconstruction again, its structure collapses under the strain of ion diffusion caused by the difference between Na⁺ and Cu⁺. This paradox highlights the severe destabilization induced by Na⁺ substitution, thereby providing a structural origin for the electronic anomalies discussed earlier.

Then, as shown in Figure 1i–k, for the pure Cu₃VS₄, the Mg²⁺ insertion and diffusion processes are significantly impeded by the restricted charge compensation, predicting that it will produce low and irreversible magnesium storage capacity. Differently, low-concentration Na⁺ doping triggers the formation of a low-spin V^{(5-x)+} ion, which promotes both electron and Mg²⁺ transport kinetics. However, although high concentrations of Na⁺ doping can induce more spin-states of V-ion (even higher spin-state), severe lattice distortion and lead to excessive Na⁺ occupying magnesium storage sites, ultimately resulting in low storage capacity. Moreover, the Na⁺ located at the Cu⁺ site will not be beneficial for the electron transport according to the above results.

Subsequently, ab initio molecular dynamics (AIMD) simulations were employed to evaluate the thermodynamic stability of the

mentioned structures (Calculated by the DS-PAW software[48] in DeviceStudio-2023 from HZWTECH, Figures S18 and S19). The results indicate that the total energy exhibits only minor fluctuations in the Na-0 to Na-5 series, whereas pronounced oscillations are observed for Na-5-2, revealing its substantial structural instability. Furthermore, the steadily increasing root-mean-square deviation (RMSD) over simulation time confirms that Na⁺ incorporation gradually degrades structural integrity (Figure S20). Specifically, in Na-5-2, certain Na⁺ migrate from the substituted Cu⁺ sites into interstitial positions, ultimately leading to structural collapse.

Therefore, theoretical calculations reveal that Na⁺ preferentially occupies the interstitial sites of Cu₃VS₄ and modulates the electronic structure after occupying the e_g orbital, thereby achieving consistent adsorption strength and low diffusion barriers. Moreover, the doping concentration of Na⁺ is expected to exhibit a volcano-type relationship in influencing the magnesium storage performance.

2.2 | Material Synthesis and Characterization

Based on the above discussion, varying molar amounts of Na⁺ were introduced into Cu₃VS₄ via a simple solvothermal method (denoted as N-0, N-0.5, N-1.5, and N-3, Figure S21). As shown in Figure 2a, with increasing Na⁺ content, the XRD peak intensities gradually weakened, and the peak positions shifted to lower angles, but a new phase had appeared when the Na⁺ content was increased to 3.7 mmol, as shown in Figure S22. Notably, within the lower doping range, no impurity peaks were detected, suggesting that Na⁺ incorporation, enabled by its larger ionic radius, only expanded the interlayer spacing while preserving the host crystal structure. This result is further supported by Raman spectroscopy (Figure S23), which could be attributed to the fact that Na⁺ ions in excessive amounts induce the structural collapse of Cu₃VS₄ and the formation of unexpected phases. According to ICP results normalized to the sulfur content (Figure S24), the Na⁺ content increased substantially overall. Minor variations were observed in samples N-0, N-0.5, and N-1.5, which can be ascribed to the use of the surfactant SDS as the sodium source. In contrast, a notable decrease in Cu content was detected in sample N-3, suggesting the occurrence of cation mixing between Na⁺ and Cu⁺, where Na⁺ substitutes for Cu⁺ at lattice sites.

As the amount of the Na⁺ source increased, the morphology of the samples evolved gradually from microspheres to irregular flake-like particles. All the prepared samples—N-0, N-0.5, N-1.5, and N-3—displayed a homogeneous elemental distribution, as shown in Figures S25–S29. Furthermore, HRTEM analysis of typical samples (N-0 and N-0.5) revealed that Na⁺ incorporation induced structural disordering in Cu₃VS₄ (Figure S30). Also, the intensities of these peaks are consistent with the predicted configuration of sodium interstitial sites from multislice/frozen-phonon simulations (Figure 2b,c). Subsequently, the HAADF-STEM images confirm the high purity of the synthesized material, and the intensity line profile derived from the white dashed line in Figure 2e reveals weak peaks at the curve's trough positions (Figure 2b–e; Figure S31). Weak intensity peaks are observed at the trough positions of the curve, and the peak intensities are consistent with the predicted configuration of sodium interstitial

sites based on simulations of HAADF images using the multi-slice method and frozen-phonon approximation, which is consistent with DFT calculations and the XRD results.

XPS results provided further insight into the electronic structure evolution with Na⁺ doping. As shown in Figure S32a, the Na 1s peak gradually shifted toward higher binding energy as the Na⁺ content increased. Correspondingly, the S 2p peaks initially shifted to lower binding energies before moving back to higher values, accompanied by a gradual reduction in the proportion of S₂^{2−} species (Figure 2f) [37, 38]. The V 2p spectra (Figure 2g) were dominated by the V⁵⁺ oxidation state in sample N-0, with minor contributions from lower oxidation states (+3 and +4). In contrast, samples N-0.5 and N-1.5 exhibited a predominant V³⁺ state. However, in the high Na⁺-content sample N-3, the V⁵⁺ state again became dominant, though its relative proportion remained lower than that in N-0. Meanwhile, the Cu 2p oxidation state showed negligible variation across all samples (Figure S32b). Additionally, both S 2p and V 2p peaks in N-1.5 shifted slightly to higher binding energy compared to those in N-0.5. These spectral shifts suggest that increasing Na⁺ content progressively modifies the local coordination environment. In N-0.5, Na⁺ ions primarily occupy interstitial sites. As the doping level rises, cation mixing between Na⁺ and Cu⁺ begins to occur, being more pronounced in N-3 compared to N-1.5.

Additionally, V K-edge XANES analysis reveals a shift toward lower energy in sample N-0.5 compared to N-0 (Figure 2h–i), indicating that Na⁺ incorporation modifies the electronic structure and effectively reduces the vanadium valence state. Notably, N-0.5 exhibits a stronger pre-edge peak than N-0, suggesting lower local symmetry and enhanced distortion of the [VS₄] tetrahedral coordination [39, 40]. Differently, Cu K-edge XANES spectra show slightly variation between N-0 and N-0.5 (Figure S33), implying minimal influence on the copper sites due to the [Ar]3d¹⁰4s⁰ structure. EELS analysis further confirms the reduction in vanadium valence, as evidenced by a shift of the V 2p peak to lower energy in N-0.5 relative to N-0 (Figure S34). Additionally, as shown in Figure S35, the M-H curve demonstrated that, compared to N-0, N-0.5 exhibits a more distinct hysteresis loop; specifically, the magnetization in N-0.5 is non-zero when the magnetic field is zero. This could provide direct probes of the local electronic structure and spin information of V. Moreover, XPS-UPS measurements reveal valence band positions of 3.47 eV for N-0 and 3.20 eV for N-0.5 (Figure S36), indicating that Na⁺ pre-intercalation narrows the band gap—a result consistent with DFT calculations.

The above characterization of the electronic structure confirms that Na⁺ could modify the electronic structure of S 3p, leading to a subsequent electron filling and rearrangement of the V-3d orbital, thus verifying the consistency with the theoretical calculations.

2.3 | Electrochemical Reconstruction and Characterization

Usually, electrochemical reconstruction can induce a transformation in the crystal structure of the material for favorable charge ion insertion/extraction during the cycling process under the stress effect and others [41–43]. First, the CV curves shown

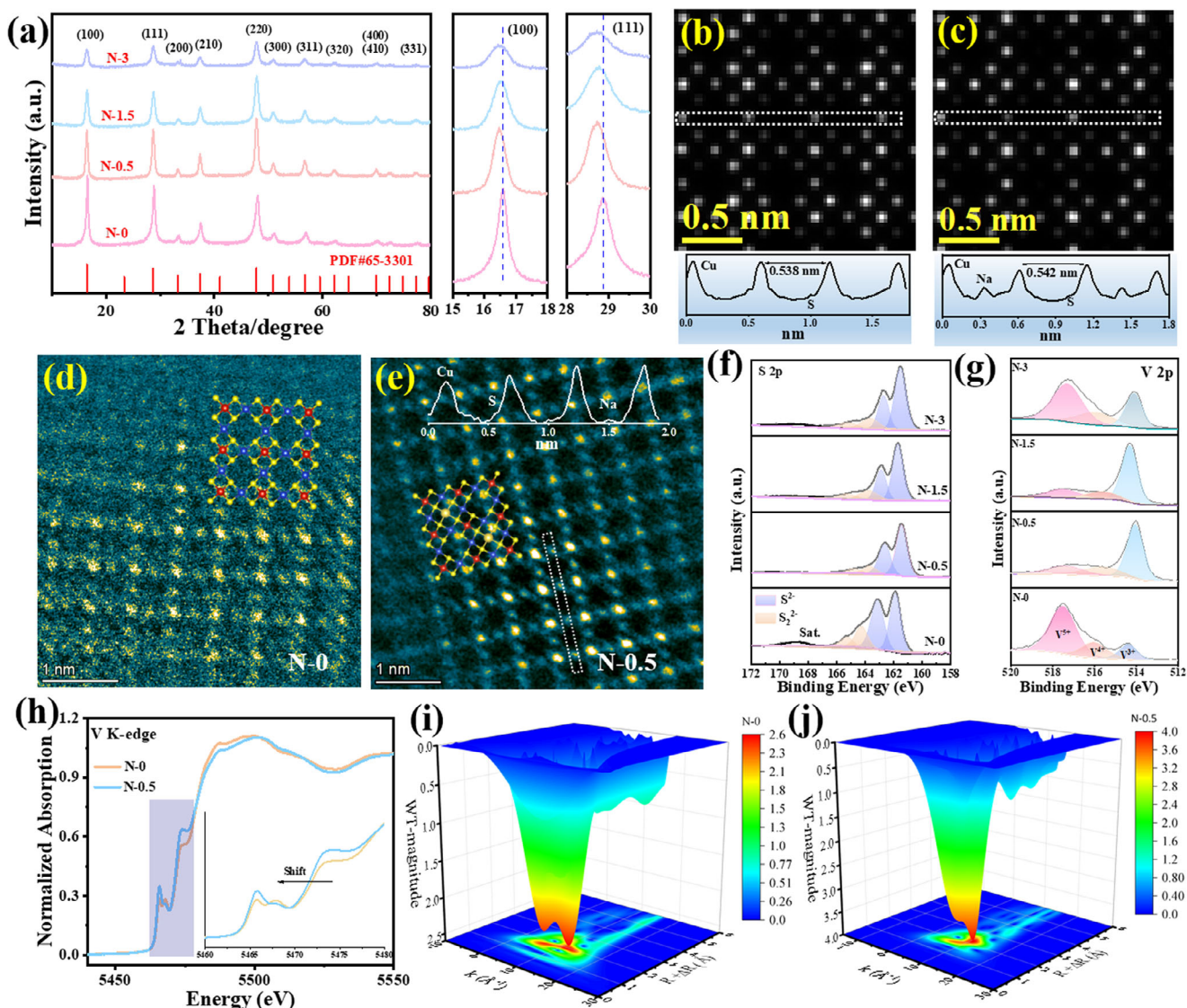


FIGURE 2 | (a) XRD patterns of Cu_3VS_4 with different concentrations of Na^+ ion doping (N-0, N-0.5, N-1.5, and N-3). (b–e) Experimental and simulated aberration-corrected TEM images of N-0 and N-0.5. (f,g) XPS spectra of S 2p and V 2p. (h–j) V K-edge XANES of the N-0 and N-0.5 and the corresponding WT-EXAFS.

in Figure S37 indicate that samples N-0 and N-3 exhibit weak current, whereas N-0.5 and N-1.5 demonstrate behavior of increased peak current, with the latter showing higher peak currents. This preliminarily suggests that an appropriate concentration of Na^+ unlocks the magnesium storage capability of Cu_3VS_4 .

To further evaluate the electrochemical transformation, the four cathode materials were cycled 100 times at a low current density of 40 mA g^{-1} . As depicted in Figure 3a, all samples show a discharge plateau near 1.4 V during the initial cycle, corresponding to the reduction of high-valence vanadium. In contrast, the Na^+ -doped samples (N-0.5, N-1.5, and N-3) exhibit an additional plateau around 0.5 V, associated with low-valence vanadium, though it is less pronounced in N-3. During charging, N-0.5 and N-1.5 show more defined plateaus near 1.6 V compared to N-0 and N-3. Among all samples, N-1.5 delivers the highest specific capacity, attributable to its higher Na^+ content.

A schematic illustration of the Mg^{2+} storage behavior of the four materials during initial cycling is presented in Figure 3b. In N-0 and N-3, the high ratio of high-valence vanadium results in severe surface passivation, owing to sluggish charge compensation and strong electrostatic repulsion between V^{5+} and Mg^{2+} , which hinders Mg^{2+} diffusion. In N-3, excessive Na^+ ions not only occupy Mg^{2+} sites but also intensify electrostatic blocking, further limiting Mg^{2+} storage. In contrast, N-0.5 and N-1.5—with moderate Na^+ doping—contain more V^{3+} , which improves electron transfer and facilitates Mg^{2+} intercalation, thereby mitigating passivation and enabling a reversible Mg^{2+} insertion/extraction process [44, 45]. The higher Na^+ content in N-1.5 further enlarges the reversible reaction region.

In subsequent cycles, all electrodes exhibit increasing capacities and more distinct redox plateaus (Figure 3c; Figures S38 and S39). However, their activation behaviors differ: N-1.5 shows the most pronounced activation, reaching its maximum capacity by the 70th cycle but then decaying rapidly. Although N-0.5 also

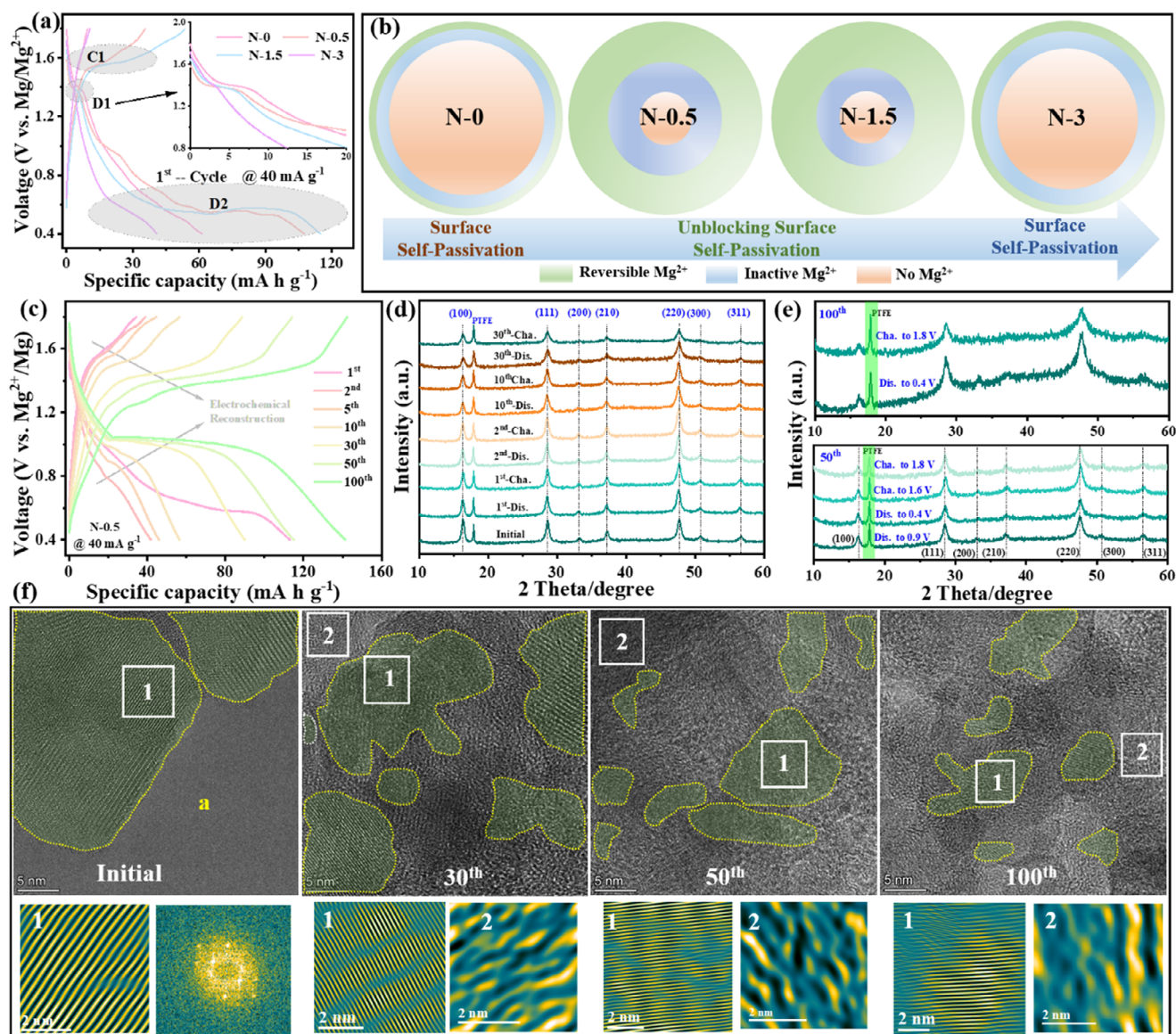


FIGURE 3 | (a,b) Comparison of the initial charge–discharge curves of four cathode materials and the corresponding schematic diagrams of their magnesium storage activity and reversibility. (c) Charge–discharge curves of N-0.5, and (d,e) Ex situ XRD patterns of N-0.5 during the first 100 cycles of electrochemical reconstruction, as well as (f) the corresponding schematic diagrams of crystal structure evolution.

undergoes noticeable activation, its capacity peaks only after 100 cycles. By contrast, N-0 and N-3 maintain low specific capacities throughout. Owing to its higher fraction of low-valence vanadium, N-3 delivers a higher capacity and a clearer discharge plateau than N-0. When the areal loading of the electrode increases to 5.2 mg cm^{-2} , an electrochemical activation process and unlocked capacity were still observed and had same redox plateaus (Figure S40). However, the specific capacity is slightly lower than that under lower loadings after 50 cycles. This is attributed to the increased reaction depth, where thicker electrodes lead to longer electron conduction and ion diffusion paths, and increased internal resistance. The above electrochemical results convincingly demonstrate that Na^+ ions can induce the electrochemical reactivity, and only an optimal concentration of Na^+ doping can not only facilitate the electrochemical reaction process but also contribute to maintaining a stable cycling process.

Subsequently, as shown in Figure S41, N-0 showed no significant diffraction peak attenuation or shift during the initial cycling process according to ex-situ XRD, and the ex-situ Raman demonstrated that minor Mg^{2+} could participate in the storage process. Further, the ex-situ XPS result shows that although signals of common Mg^{2+} and Cl^- were detected in N-0 (Figure S42) [46], the reactive elements remained consistent with those in the uncycled electrode in both fully discharged and charged states, indicating that only minimal adsorption of Mg^{2+} occurred on the surface of N-0.

Subsequently, although the XRD patterns of N-0.5 in the initial cycles did not show significant peak shifts in Figure S43, the peak intensities gradually weakened as cycling progressed, particularly after 50 and 100 cycles (Figure 3d,e). Notably, it can be seen from Figure S44 that the fraction of amorphization increased from 4.53 % at the initial state to 92.5 % at the 100th cycle. Subsequently, this

attenuation was further corroborated by ex-situ TEM analysis, which directly revealed a progressive reduction in crystalline domains (Figure 3f). Accompanying this change was the emergence of a disordered structure, collectively indicating a transition toward co-existing nanocrystalline/amorphous configuration—consistent with the electrochemical evolution and the ex-situ XRD trends.

Furthermore, ex-situ XPS results indicated that Mg^{2+} and Cl^- species exhibited highly reversible behavior over the 100 cycles, while the Na^+ signal remained relatively stable (Figures S45 and S46). In the initial cycles, vanadium and sulfur also displayed reversible changes corresponding to Mg^{2+} insertion/extraction, with copper showing negligible variation (Figures S47 and S48). However, as cycling proceeded, these reversible features became less distinct, likely due to the progressive amorphization; despite this, the vanadium predominantly maintained a V^{3+} species. Throughout these structural changes, ex-situ ICP analysis confirmed that Mg^{2+} storage remained highly reversible (Figure S50).

Based on the above discussion, the driving force for the electrochemical reconstruction primarily stems from the intrinsic stress induced by Na^+ doping, as well as the subsequent stress changes caused by electrostatic interactions during Mg^{2+} insertion and diffusion, ultimately leading to an adaptive structural transformation. Specifically, this process transforms the material from a well-crystalline state into a microcrystalline/amorphous composite structure within 100 cycles (named as C@A-N-0.5, Figure 4a). The microcrystalline regions within this adaptive architecture help reduce excessive grain boundaries, thereby shortening diffusion pathways while preserving the electronic conductivity inherent to the crystalline framework—both of which facilitate Mg^{2+} transport. Meanwhile, the amorphous phase significantly increases the exposure of more active sites and alleviates stress induced by Mg^{2+} diffusion, which is crucial for maintaining long-term cycling stability. Typically, the Mg^{2+} diffusion coefficient could achieve $2.07 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ at the 50th cycle (Figure S51).

Furthermore, Density Functional Theory (DFT) calculations were performed to assess the advantages of the amorphous structure for Mg^{2+} storage in Na-2 and Na-5 configurations, which correspond to low and high Na^+ doping concentrations in Cu_3VS_4 , respectively. Comparison of the Mg^{2+} adsorption energies at two distinct sites shows relatively similar values in Na-2, whereas significant differences are observed in Na-5 (Figure 4b), suggesting that Na-2 may provide more favorable diffusion pathways for Mg^{2+} . Moreover, fitting of the mean-squared-displacement (MSD) curves indicates that the Mg^{2+} diffusion rate in Na-2 is approximately 7 times higher than that in Na-5 (Figure 4c). This discrepancy is mainly due to the excessively high Na^+ content in Na-5, which blocks Mg^{2+} migration pathways and helps explain the poor cycling stability of N-1.5 observed experimentally.

In-situ EIS was employed to investigate the evolution of the cathode/electrolyte interface during electrochemical reconstruction (Figure 4d,e; Figure S52). The impedance in the high-frequency region is mainly influenced by charge transfer kinetics, while the low-frequency region is dominated by mass transport [47].

Specifically, P1 corresponds to the contact resistance at the current collector/electrode interface and between electrode particles. P2 reflects interfacial polarization and ion adsorption/desorption kinetics. P3 is associated with electron transport within the active material. P4 is related to the migration of Mg^{2+} at the cathode surface. P5 represents the mid-frequency semicircle related to charge transfer, and P6 corresponds to the low-frequency slope, indicating solid-state diffusion of Mg^{2+} . The DRT projection map shows a clear decrease in the intensity of all six peaks, which is mainly attributed to the microcrystalline/amorphous transformation reducing grain boundaries, creating an environment with more active sites, improved ion pathways, and a more stable interface, thereby significantly reducing interfacial impedance. Meanwhile, TOF-SIMS analysis demonstrated that the Na^+ content remains largely stable, while the Mg^{2+} concentration varies reversibly over each full charge–discharge cycle (Figure 4f; Figure S53). These findings are further supported by ex-situ ICP measurements, which confirm the stability of Na^+ during the electrochemical reconstruction process (Figure S54).

2.4 | Electrochemical Performance and Energy Storage Mechanism

The electrochemically reconstructed cathode material, C@A-N-0.5, exhibited a specific capacity of 140 mAh g^{-1} at 40 mA g^{-1} (Figure 5a). Differently, the N-0 still delivers negligible capacity, even though it was activated after 100th cycles, which not only demonstrates that the origin of the capacity is closely associated with the spin state of vanadium, but also reveals that the structural adaptive transformation occurs only with Na^+ -doping. Crucially, the capacity decay process did not commence until after 300 cycles. Furthermore, the corresponding galvanostatic charge–discharge (GCD) curves demonstrated highly overlapping profiles, indicating that C@A-N-0.5 possesses excellent structural stability and no longer undergoes significant structural transformation (Figure 5b). Additionally, C@A-N-0.5 delivered considerable specific capacities and distinct voltage plateaus at various current densities (Figure 5c,d). Finally, C@A-N-0.5 maintained a high specific capacity exceeding 100 mAh g^{-1} , which simultaneously exhibits considerable specific capacity and remarkable cycling stability when compared to existing sulfides (Table S1). It also exhibited a satisfactory capacity retention after 1000 cycles at a high current density of 200 mA g^{-1} (Figure 5e). The above cycling performance results clearly demonstrate that the electrochemically reconstructed C@A-N-0.5 exhibits superior structural stability and a highly reversible cycling process.

Subsequently, ex-situ XRD and Raman spectroscopy confirmed that C@A-N-0.5 maintains the characteristic diffraction peaks of Cu_3VS_4 during the Mg^{2+} intercalation/deintercalation process, demonstrating a crystal structure characterized by the coexistence of microcrystalline and crystalline forms (Figure S55). Furthermore, ex-situ TEM mapping revealed that the content of Mg^{2+} and MgCl^+ is significantly higher during the discharge process compared to the subsequent charging process, confirming the reversible insertion/extraction mechanism of Mg^{2+} and MgCl^+ within the C@A-N-0.5 (Figure 5f; Figure S56). Additionally, HRTEM images further corroborated the stability of the microcrystalline/crystalline coexistence structure at fully charged states (Figure S57).

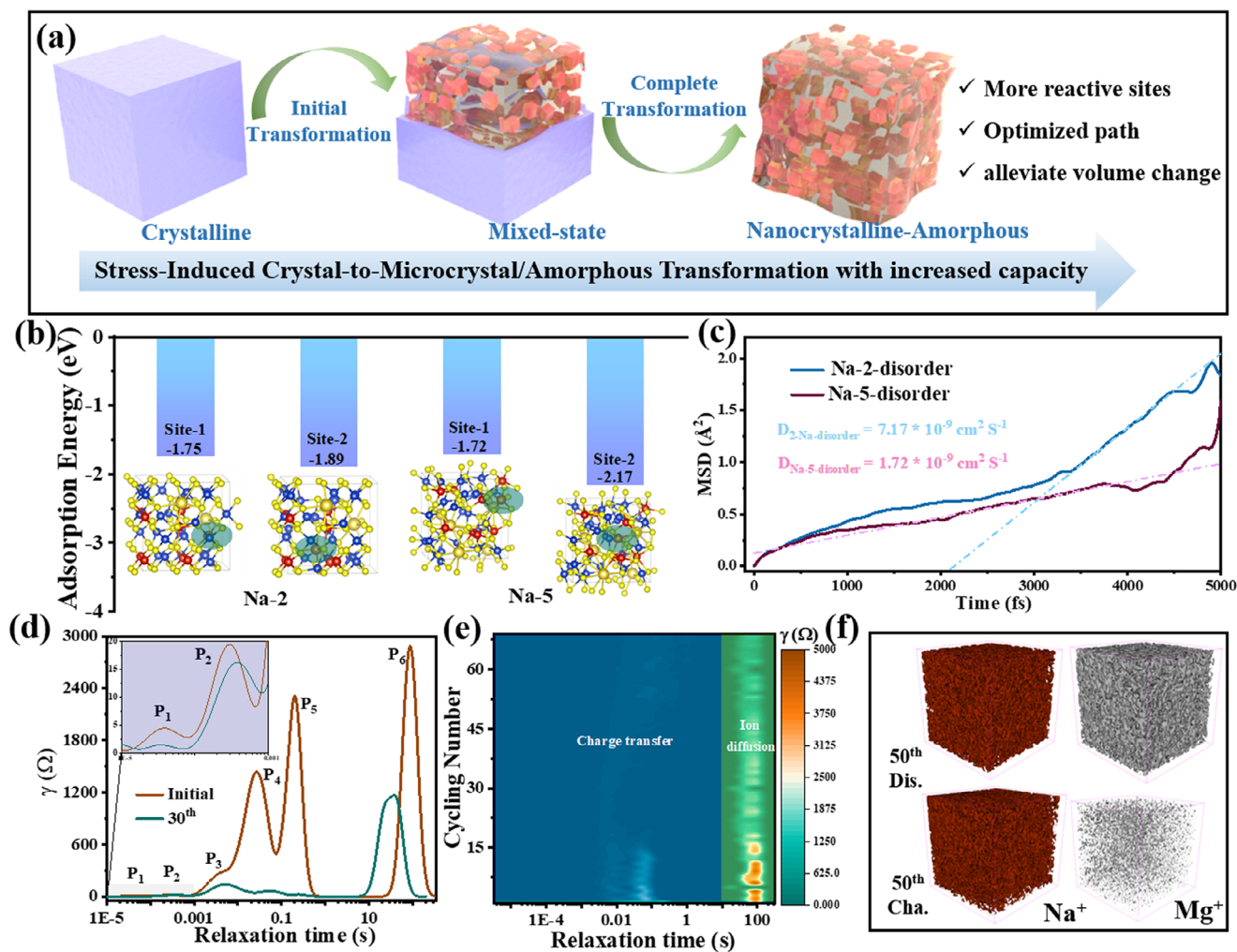


FIGURE 4 | (a) Schematic diagram of the crystal structure evolution of N-0.5 during electrochemical reconstruction. (b,c) Comparison of the adsorption energies of Mg^{2+} ions in Na-2 and Na-5, and the corresponding mean square displacement (MSD) curves (Two disordered models were generated via variable-temperature annealing using AIMD simulations). (d,e) In situ electrochemical impedance spectroscopy (EIS) plots. (f) 3D time-of-flight secondary ion mass spectrometry (3D TOF-SIMS) mapping of Na^+ and Mg^{2+} ion distributions in N-0.5 at the fully discharged and charged states in the 50th cycle.

As summarized from the discussion above, the schematic diagram illustrates the Mg^{2+} storage mechanism in C@A-N-0.5 (Figure 5g). The V^{3+} spin state induced by Na^+ doping plays a continuing role in facilitating electron transport, while the microcrystalline structure upholds the conductive benefit of the crystalline phase. Concurrently, the stress-induced microcrystalline/amorphous structure helps alleviate mechanical strain and provides additional active sites for the reversible adsorption/desorption of Mg^{2+} . Such a synergistic effect enables well-coordinated electron and Mg^{2+} transport, which ensures efficient charge balance and facilitates stable electrochemical cycling.

3 | Conclusion

In conclusion, to address the challenge of sluggish insertion/diffusion of highly polar Mg^{2+} in cathode materials, the synergistic strategy has been proposed involving the modulation of both electronic and crystal structures to resolve the inherent conflict between thermodynamic stability and ionic transport

kinetics. It is demonstrated that the introduction of Na^+ precisely regulates the electron occupancy of the V-3d orbital in Cu_3VS_4 , thereby optimizing the Mg^{2+} adsorption energy and facilitating the charge transfer process. Ex-situ XRD, XPS, TEM, and in-situ EIS analyses further confirm that the intrinsic lattice strain induced by Na^+ doping, combined with cyclic stress, triggers an electrochemical reconstruction, resulting in a novel microstructure characterized by a microcrystalline/amorphous composite for optimizing the Mg^{2+} adsorption and diffusion process. This synergistic approach significantly mitigates cathode surface self-passivation caused by the irreversible Mg^{2+} ion, enabling the modified Cu_3VS_4 to transition from being nearly inactive to exhibiting remarkable rate capability and cycling stability. These results validate the effectiveness of combining electronic-level modulation (mainly optimizing adsorption behavior) with structural-level engineering (mainly enhancing diffusion process). From the perspective of synergistic electron/ion transport mechanisms, this study provides new insights and a feasible direction for developing high-performance cathode materials for multivalent ion batteries.

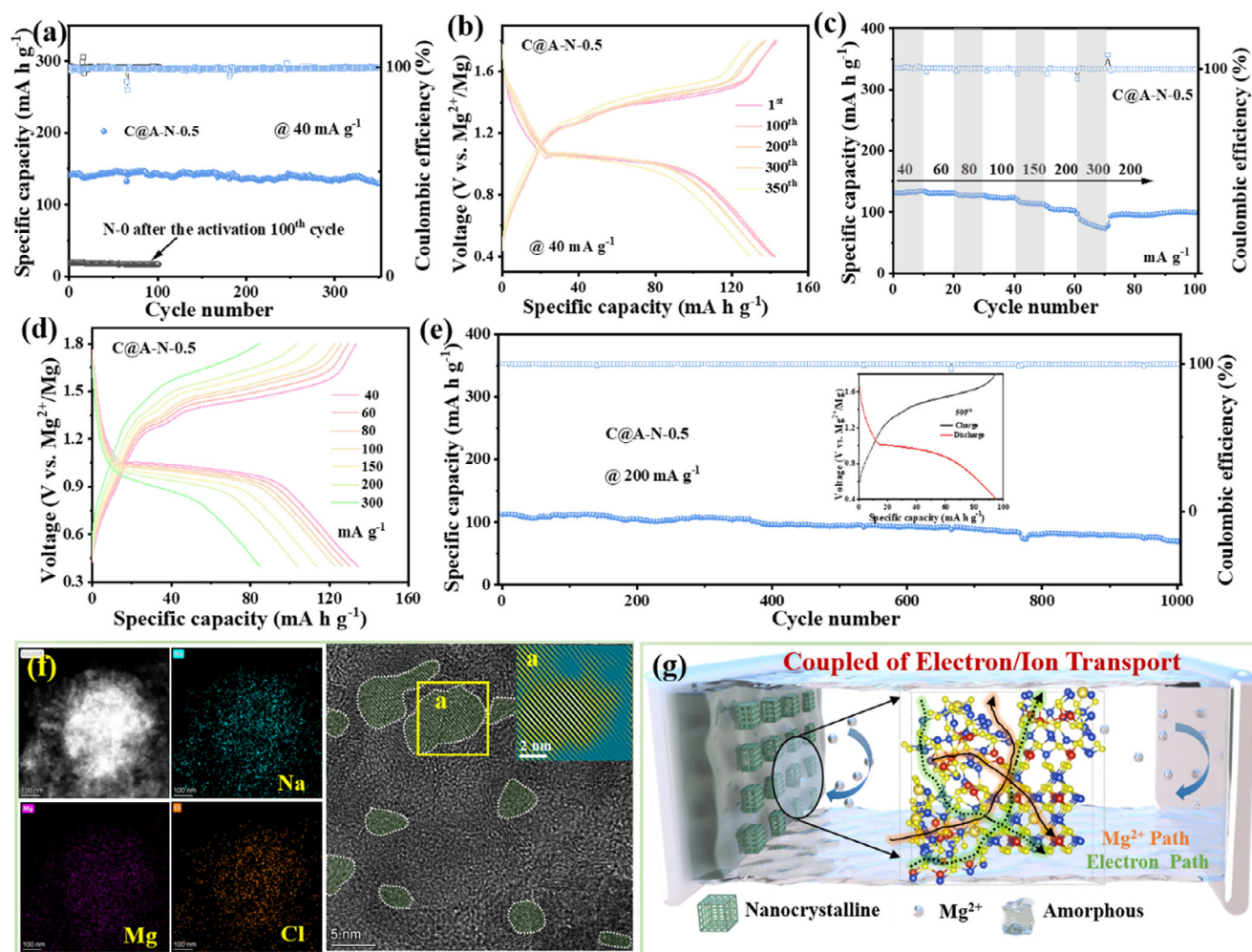


FIGURE 5 | (a,b) Cycling performance of C@A-N-0.5 at 40 mA g⁻¹ and the corresponding charge–discharge curves. (c,d) Rate capability of C@A-N-0.5 at different current densities and the corresponding charge–discharge curves. (e) Cycling performance of C@A-N-0.5 at 200 mA g⁻¹. (f) TEM elemental mapping and HRTEM images of C@A-N-0.5 at the fully discharged state of the 6th cycle. (g) Schematic illustration of magnesium storage in C@A-N-0.5.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article.

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